Statistical Thermodynamics in Chemistry and Biology

19. Chemical kinetics and transition states

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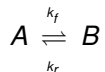*per-olof.aastrand@ntnu.no*

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Rates of chemical reactions

This chapter:

▶ Rate constants for reactions are connected to equilibrium constants (Chapter 13)

▶ Add one additional concept: *transition state* or *activation barrier*

▶ Chemical reactions are strongly temperature-dependent

Reaction rates are proportional to concentrations

- A reaction,

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

  where k_f and k_r are rate constants for the forward and reverse reactions, respectively.

- The rates are given as

$$\frac{d[A(t)]}{dt} = -k_f[A(t)] + k_r[B(t)]$$

$$\frac{d[B(t)]}{dt} = k_f[A(t)] - k_r[B(t)]$$

  where $[A(t)]$ is the concentration (or number of particles) at time t.

- Rate constants k_f have the unit of inverse time (frequency).

- Coupled differential equations that can be solved by standard matrix techniques.

Reaction rates are proportional to concentrations
Part 2

▶ In many cases, the reverse reaction may be neglected $k_r \ll k_f$,

$$\frac{d[A(t)]}{dt} = -k_f[A(t)]$$

which has the solution,

$$[A(t)] = [A(0)]e^{-k_f t}$$

▶ An *exponential decay*.
▶ [B] changes as,

$$[B(t)] = [B(0)] + [A(0)]\left(1 - e^{-k_f t}\right)$$

At equilibrium

- At equilibrium, the change in concentrations are zero,

$$\frac{d[A(t)]}{dt} = \frac{d[B(t)]}{dt} = 0$$

- It results in the principle of detailed balance,
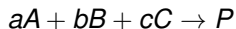
$$k_f[A]_{\text{eq}} = k_r[B]_{\text{eq}}$$

which may be rewritten as

$$K = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k_f}{k_r}$$

where K is the equilibrium constant.

The mass action law – Guldberg-Waage law

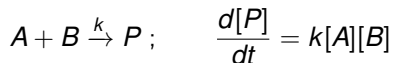- Suppose we have a chemical reaction,

$$aA + bB + cC \rightarrow P$$

- The law of mass action:

$$\frac{d[P]}{dt} = k_f[A]^a[B]^b[C]^c$$

- The stoichiometric coefficients (the mechanisms of reactions) are thus available from kinetics experiments.

Temperature dependence on reaction rates

▶ Consider the binary reaction,

$$A + B \xrightarrow{k} P \; ; \qquad \frac{d[P]}{dt} = k[A][B]$$

▶ k is assumed to be independent of the concentrations, but may be strongly dependent on the *temperature*.

▶ Based on the van't Hoff equation (Eq. 13.35),

$$\frac{d \ln K}{dT} = \frac{\Delta h^o}{k_B T^2}$$

Arrhenius suggested for the rate constants,

$$\frac{d \ln k_f}{dT} = \frac{E_a}{k_B T^2} \; ; \qquad \frac{d \ln k_r}{dT} = \frac{E_a'}{k_B T^2}$$

▶ E_a and E_a' are termed activation energies.

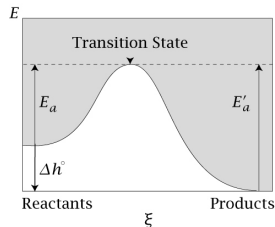# Transition states

- The concept of transition state or activation barrier is introduced.
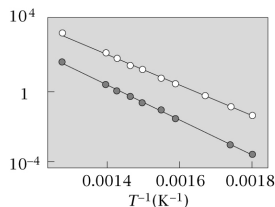- Integrating the equation above gives the Arrhenius equation,

$$k_f = Ae^{-\beta E_A}$$

  where A is a constant that can be determined by kinetics experiments at different temperatures.

- In experiment, A and E_A are determined by plotting $\ln k_f$ against $1/T$ (see figure to the right).
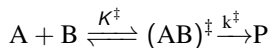
Transition state theory

Only sketched briefly

- In transition state theory, the reaction is divided into two steps,

$$\text{A} + \text{B} \underset{}{\overset{K^{\ddagger}}{\rightleftharpoons}} (\text{AB})^{\ddagger} \overset{k^{\ddagger}}{\longrightarrow} \text{P}$$

- $(AB)^{\ddagger}$ denotes the complex formed at the transition state.
- The first step is the equilibrium between the reactants and the transition state described by the equilibrium constant $K^{\ddagger}$.
- The second step, downhill from the transition state, is described by the rate coefficient, $k^{\ddagger}$.
- The equilibrium constant, $K^{\ddagger}$, is given as

$$K^{\ddagger} = \frac{[(AB)^{\ddagger}]}{[A][B]}$$

- The overall rate, k, may be introduced as

$$\frac{d[P]}{dt} = k^{\ddagger}[(AB)^{\ddagger}] = k^{\ddagger} K^{\ddagger}[A][B] = k[A][B]$$

Transition state theory

Part 2

▶ Expressing $K^{\ddagger}$ in terms of the partition function (eq. 13.17),

$$K^{\ddagger} = \frac{q_{(AB)^{\ddagger}}}{q_A q_B} e^{\frac{\Delta D^{\ddagger}}{k_B T}}$$

and factorizing $q_{(AB)^{\ddagger}} = \overline{q^{\ddagger}} q_{\xi}$ where q_{ξ} is the partition function for the motion along the reaction coordinate.

▶ Skipping the details...

$$K^{\ddagger} = \overline{K^{\ddagger}} q_{\xi} \approx \overline{K^{\ddagger}} \frac{k_B T}{h \nu_{\xi}}$$

where ν_{ξ} is a vibrational frequency along the reaction coordinate. Also skipping the details, the rate constant for the second step,

$$k^{\ddagger} \approx \nu_{\xi}$$

▶ The entire rate constant k is given as

$$k = k^{\ddagger} K^{\ddagger} = \frac{k_B T}{h} \frac{\overline{q^{\ddagger}}}{q_A q_B} e^{\frac{\Delta D^{\ddagger}}{k_B T}} = \frac{k_B T}{h} \overline{K^{\ddagger}}$$

where $\overline{K^{\ddagger}}$ is termed the activation equilibrium constant.

Thermodynamics of the activated state

▶ Relate the activation equilibrium constant, $\overline{K^{\ddagger}}$, to the activation free energy, $\Delta G^{\ddagger}$,

$$-k_B T \ln \overline{K^{\ddagger}} = \Delta G^{\ddagger} = \Delta H^{\ddagger} - T \Delta S^{\ddagger}$$

where $\Delta H^{\ddagger}$ is the activation enthalpy and $\Delta S^{\ddagger}$ is the activation entropy.

▶ Using the result for the rate constant, k, from transition state theory,

$$k = \frac{k_B T}{h} \overline{K^{\ddagger}} = \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{k_B T}} = \frac{k_B T}{h} e^{-\frac{\Delta H^{\ddagger}}{k_B T}} e^{\frac{\Delta S^{\ddagger}}{k_B}}$$
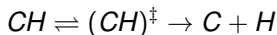
▶ Comparing to the Arrhenius equation,

$$k_f = A e^{-\beta E_A}$$

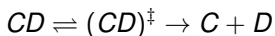leads to that the A-term in Arrhenius equation can be identified

$$A = \frac{k_B T}{h} e^{\frac{\Delta S^{\ddagger}}{k_B}}$$

The primary isotope effect

- Isotope substitution is useful for determine reaction mechanisms.
- For example, at room temperature the C-H bond cleaves 8 times faster than a C-D bond.
- This will be explained by an example. Comparing

$$CH \rightleftharpoons (CH)^{\ddagger} \to C + H$$

with the rate constant k_H, and

$$CD \rightleftharpoons (CD)^{\ddagger} \to C + D$$

with the rate constant k_D and D denotes deuterium ^2H.

- Use previous result for the rate constant, k,

$$k = \frac{k_B T}{h} \frac{\overline{q^{\ddagger}}}{q_A q_B} e^{\frac{\Delta D^{\ddagger}}{k_B T}}$$

The primary isotope effect
Part 2

▶ The ratio of the reaction rates becomes

$$\frac{k_H}{k_D} = \frac{\frac{q_{CH}^\ddagger}{q_{CH}} e^{\frac{\Delta D_{CH}^\ddagger}{k_B T}}}{\frac{q_{CD}^\ddagger}{q_{CD}} e^{\frac{\Delta D_{CD}^\ddagger}{k_B T}}} \approx e^{\frac{\Delta D_{CH}^\ddagger - \Delta D_{CD}^\ddagger}{k_B T}}$$

where we now use the notation $q_{CH}^\ddagger$ instead of $\overline{q^\ddagger}$.

▶ The difference in dissociation energies is the difference in ground-state energies. The electronic states are the same for CH and CD, whereas the vibrational ground-state energy, the zero-point vibrational energy differs.

▶ At the transition state, the bond breaks (not vibrating), so it is only the zero-point vibrational energy for the reactants that are affected,

$$\Delta D_{CH}^\ddagger - \Delta D_{CD}^\ddagger = -\frac{1}{2} h(\nu_{CD} - \nu_{CH})$$

where ν is a vibrational frequency.

The primary isotope effect
Part 3

▶ Regard the reduced masses,

$$\mu_{CH} = \frac{m_C m_H}{m_C + m_H} \approx m_H \; ; \qquad \mu_{CD} = \frac{m_C m_D}{m_C + m_D} \approx m_D \approx 2m_H \approx 2\mu_{CH}$$

▶ The force konstant, k_s is the same for CH and CD, giving the frequency,

$$\nu_{CD} = \frac{1}{2\pi}\sqrt{\frac{k_s}{\mu_{CD}}} \approx \frac{1}{2\pi}\sqrt{\frac{k_s}{2\mu_{CH}}} = \frac{\nu_{CH}}{\sqrt{2}} \; ; \qquad \nu_{CD} - \nu_{CH} = \left(\frac{1}{\sqrt{2}} - 1\right)\nu_{CH}$$
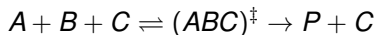
▶ This leads to the final result

$$\frac{k_H}{k_D} = \exp\left(\frac{-h\nu_{CH}}{k_B T}\left(\frac{1}{\sqrt{2}} - 1\right)\right)$$

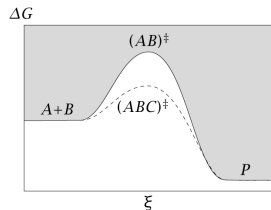▶ Example 19.3: For $\nu_{CH} = 2900$ cm^{-1} and at $T = 300$ K, we get $\frac{k_H}{k_D} = 7.68$.

Catalysis

▶ Pauling suggested that catalysts work by stabilization of the transition state.

▶ A catalyzed reaction (C is not consumed),

$$A + B + C \rightleftharpoons (ABC)^{\ddagger} \rightarrow P + C$$

▶ Two reaction rates, k_c for the catalyzed reaction and k_0 without a catalyst,

$$\frac{k_c}{k_0} = \frac{\overline{K_c^{\ddagger}}}{K_0^{\ddagger}} = \frac{[(\overline{ABC})^{\ddagger}]}{[(\overline{AB})^{\ddagger}][C]} = \overline{K}_B$$
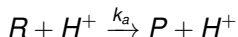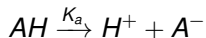
where the equilibrium constant, $\overline{K}_B$ is referred to as a binding constant.

The Brønsted law

. . . of acid (base) catalysis - used in chapter 28

▶ The stronger the acid, the faster the reaction it catalyzes.

$$AH \xrightarrow{K_a} H^+ + A^-$$

$$R + H^+ \xrightarrow{k_a} P + H^+$$

with

$$K_a = \frac{[H^+][A^-]}{[AH]}$$

▶ Let's write (alternative $\propto [H^+][R]$),

$$\frac{d[R]}{dt} = -k_a[AH][R]$$

The Brønsted law
Part 2

▶ Brønsted law is an observation,

$$\ln k_a = \alpha \ln K_a + c_a$$

where c_a and $\alpha > 0$ are constants.

▶ With $pK_a = -\ln K_a$, (analogous to pH)

$$\ln k_a = -\alpha pK_a + c_a$$

▶ Implies a linear free-energy relationship of the form

$$E_a = a\Delta G + b$$

where E_a is the activation barrier and $\Delta G = -k_B T \ln K_a$ is for the acid dissociation. a and b are constants.

▶ Motivated in the Evans-Polanyi model (in the book, but not included in the course)

Summary

► Introduction to chemical kinetics

► Concepts like rate constants and their relation to equilibrium constants.

► Temperature-dependence on rate constants introduced through Arrhenius equations.

► Concepts like activation energies and transition states.

► Briefly sketched transition state theory.

► The primary isotope effect for determining reaction mechanisms

► Brief introduction to catalysis and the Brønsted law.